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outline may have been sufficient to indicate the very fundamental character of those problems.

GEOPHYSICAL LABORATORY,  
CARNEGIE INSTITUTION OF WASHINGTON.

June, 1920.

<sup>1</sup> U. S. Geol. Survey, *Prof. Paper* 85C, 1913 (35).

<sup>2</sup> See Lambert, *Journ. Wash. Acad. Sci.*, 10, 1920 (122-143).

<sup>3</sup> In this connection it is important that the study of the composition and probable sources of the matter now being received by the earth, in the form of stony and metallic meteorites, be continued and extended.

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## THE IONIZATION OF STRONG ELECTROLYTES

BY WILLIAM D. HARKINS

KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO

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It is well known that in all branches of knowledge it is sometimes difficult to express certain thoughts with accuracy on account of the fact that the meaning of words changes. So in science there are periods when either the same words have a dissimilar meaning, or unlike words have the same meaning, to different workers. This sometimes becomes so marked that old hypotheses may seem to disappear, or new ones to appear, when only the significance of the technical terms has undergone a change. In other cases old terms may be used in new ways to suggest valuable new points of view.

The recent paper by A. A. Noyes and D. A. MacInnes in these PROCEEDINGS<sup>1</sup> which supports the idea of Sutherland,<sup>2</sup> Milner,<sup>3</sup> Ghosh,<sup>4</sup> and Bjerrum,<sup>5</sup> that strong electrolytes are completely *ionized* in solution, may be considered as belonging to the last category. They use the term ion in the sense of a charged particle, and not as a charged particle which is free to move in the electric field, which is the older meaning of the term as applied to solutions, though it must be admitted that their use of the word is in harmony with the meaning attached to it in recent papers in physics. However, it is not the terminology, but the idea it is apt to convey to workers in various fields, which is to be the subject of attention in this short note. The idea developed by Bragg, that a solid salt consists not of a collection of molecules, but of atoms, has led to the

hypothesis that such salts are collections of polar atoms, which are often called ions.

Let us suppose that in the gaseous state in a system there are sodium atoms in combination with chlorine atoms. These pairs are molecules, since, on account of their considerable relative distance from other particles, their electromagnetic fields are largely self contained. It is probable that if such molecules remain at temperatures at which the solid salt exists, the distance of the sodium from the chlorine atom, will not be very different from the similar distance in the solid state. On the basis of the nomenclature which considers that the solid salt consists of ions alone, it might be said that the gaseous molecule is also ionized (called intra-molecular ionization by Thomson), but still remains together as a single molecular particle, though it seems preferable to use the terms presented by Lewis and Bray, and consider the molecule as polar, and as made up of polar atoms. If many of these gas molecules pass into an aqueous system, then it is probable that the polar atoms in practically all of them, will separate to greater distances than that between unlike atoms in the gaseous molecules. In any event the sodium chloride particles would not persist as molecules, since their electromagnetic fields would interact with those of the solvent (this action is commonly known as hydration or solvation). If the terminology is such that the salt is considered as 100% ionized in the solid or gaseous state, then it would be absurd to say that it is less than totally ionized in solution. However, many of the pairs of positive and negative polar particles, are so close together that they are not free to move in the electric field, and so in the accepted sense of the term, there are un-ionized or non-ionized aggregates. On the basis of the complete ionization convention these may be called *bound*, and those which are far apart, *free* ions.

From this standpoint let us consider that there exist at any instant in the solution, all degrees of firmness of binding, from ions which are far apart and almost entirely free, down to those which are most closely bound, and therefore are not ions in the accepted sense. Suppose that the problem is assigned of determining the degree of separation or of dissociation of the electrolyte. It is obvious that according to the way in which the distinction is drawn between the dissociated and undisassociated fractions, the calculated results will differ.

In order to prevent a confusion in terms in my own class work I have, for the past seven years used the expression, highly ionized salts, acids, and bases, are completely ionized or polarized in aqueous solution, but what may be considered the mean degree of separation or of dissociation, depends upon the method by which it is determined, since it is not to be expected that different measuring devices will draw the line of distinction at exactly the same place.

It is of interest in this connection to note that while in the papers previously cited the hypothesis is presented that the ionization is complete, and while according to the commonly accepted theory the ionization of such electrolytes, when uni-univalent, is about 0.85% at tenth-normal concentration, G. N. Lewis, and Lewis and Linhart,<sup>6</sup> have advanced the idea that the corresponding value is 68.4% (as calculated from the data of Hall and Harkins on sodium and potassium iodates). This they call the thermodynamic or corrected dissociation. It may, therefore be considered that such salts are 100% polarized or ionized, 85% electrolytically dissociated, and 68% thermodynamically dissociated. All of these conceptions are probably of use, and no one of them refers to the same feature of the phenomenon as any of the two others.

The confusion arises partly, as has been stated, from the attempt to consider a kinetic or a statistical problem as giving an average or mean which has no meaning from the standpoint of the condition in the solution, but has a considerable value as the basis for calculations by the use of empirical methods, as for example calculations of solubility or of electromotive force. Those who rally to the support of the complete ionization theory are doing so largely to do away with these mean values, and their endeavor is to introduce a statistical theory which shall be more closely descriptive of the phenomena. However, I wish to point out that to go over completely to this point of view at the present time, before the statistical theory has been worked out in an entirely satisfactory manner, is to lose some of the useful features of the older theory.

Only one of these features will be discussed. In 1911 I showed<sup>7</sup> that the effects of salts upon the solubility of univalent salts, are such as to almost inevitably lead to the conclusion that univalent salts ionize, or dissociate in steps, to form what were then called intermediate ions. According to Milner's general nomenclature these might be called associated ions. A calculation made by G. N. Lewis showed<sup>8</sup> that the transference and solubility results on this type of salts, could only be brought in harmony, on the assumption that the intermediate ion is so largely separated into its component ions, and that while it moves together under the influence of the electric field, it offers practically the same resistance to motion through the solution as if it were completely separated. Nevertheless, that there is such a union into an "intermediate" or associated, or possibly "complex" ion is clearly indicated by the phenomena. Noyes and MacInnes, though they do not consider this problem, seem to take the point of view that such relations can be accounted for by changes in the activities of the ions. However, the solubility relations of such salts could have been predicted from the standpoint of the intermediate-ion theory without any further knowledge of the relations other than those of the ordinary theory of solutions; but the activity concept, like other thermodynamic relations, is not specially fruitful in this particular sense,

though it is a powerful tool in many calculations where the premises are sufficiently known. In the end the complete ionization theory will undoubtedly be forced to consider in this case that the uni-univalent ion is often associated with the bivalent ion, and so will lead to the same conception as the older theory; but it may in the end be able to overcome the imperfections in the latter which are due to the fact that it ignores too greatly the kinetics of the phenomena, though it should be recognized that many of those who use the older theory are fully aware of the statistical features of the problem. In a certain sense it is probably nearer the truth to say that there is only one theory which is supported by the most advanced workers in the field, but that some of them pay attention to one set, and others to another set, of the features of the general theory, which will not be even approximately satisfactory until it is put much more completely into the form of partial differential equations.

Even though many physical chemists may dislike such a use of the term, it may be possible that the work ion will be used most largely in the sense in which it has been used by Noyes and MacInnes. In order to preserve some of the more valuable features of the older use of the term, in case this should occur, I wish to suggest that then a distinction be made, according to the suggestion made earlier in the paper, between ionization, and dissociation, the former term to be used whenever the particle becomes charged, the latter only when there is an obvious separation. Of course this does not surmount the difficulty that there are all degrees of separation, so there will be actually no such thing as a certain percentage dissociation. However, it may be said that the *apparent* percentage dissociation as determined by the conductivity or the thermodynamic method, has a definite value, which may, in certain cases, depend not only upon the experimental method employed, but also upon the additional hypotheses used in the calculation. What has been styled the unionized salt, may be called the undissociated salt. Intermediate or complex ions under the old nomenclature, may keep their older designations, or may be termed ion associates or complexes.

Unless those who speak of the complete ionization of all strong electrolytes do something of this sort, they will be plunged into difficulties if they attempt to use the energy concept (activity) to describe such phenomena as those in which the mercury and cadmium complexes seem, according to the commonly accepted view, to play an important part. They will have to explain also the slightly dissociated electrolytes, and those electrolytes in formic acid, which, although largely dissociated, follow the mass law, as has been found by Schlesinger.

It is always best when possible to devise new terms to express new ideas, since otherwise the point of view of all of the older literature is confused. It may be preferable, as has been suggested to the writer by Professor Stieglitz, to consider a gaseous salt molecule as made up of

*polar atoms*, and not of ions, and to use the term ions only in its historical sense, that is to designate particles which migrate in the electrical field.

<sup>1</sup> Noyes and MacInnes, these PROCEEDINGS, **5**, 1919; *J. Amer. Chem. Soc.*, **42**, 1920 (239).

<sup>2</sup> *London, Phil. Mag.*, Ser. 6, **14**, 1907 (3).

<sup>3</sup> *Ibid.*, **35**, 1918 (214, 354).

<sup>4</sup> *J. Chem. Soc.*, **113**, 1918 (449, 627).

<sup>5</sup> Bjerrum, *Zs. Elektrochem.*, **24**, 1918 (321).

<sup>6</sup> *J. Amer. Chem. Soc.*, **33**, 1911 (1807, 1827, 1836).

<sup>7</sup> *Ibid.*, **41**, 1919 (1951); **34**, 1912 (1631).

<sup>8</sup> *Ibid.*, **33**, 1911 (1864).

ON A CONDITION FOR HELMHOLTZ'S EQUATION SIMILAR TO  
LAMÉ'S

BY ARTHUR GORDON WEBSTER

CLARK UNIVERSITY

Communicated July 14, 1902

During the last thirty years the writer has been very much interested in the diffraction of sound, a subject suggested to him for theoretical treatment in 1888 by his teacher, the great von Helmholtz. Considering the great amount of paper spoiled in futile attempts to further the subject, the pessimistic view of Lord Rayleigh, and the amount of experimental results obtained by the writer, but not published, it seems proper, in accordance with a policy recently announced by the writer, to publish whatever he has in storage, however modest. A small attempt was made in a paper "On the Wave Potential of a Circular Line of Sources (*Proc. Amer. Acad. Arts Sci.*, December, 1911), an improvement on which has been recently made. The following paper is taken from a drawer, endorsed February 20, 1908, and like the other was written in the attempt to advance the theory of the megaphone.

The condition obtained by Lamé that a singly infinite family of surfaces shall be the equipotentials for some distribution is well known. It occurred to me to examine the condition that there may be a function  $V$  satisfying the differential equation investigated by von Helmholtz,

$$\Delta V + k^2 V = 0, \quad (1)$$

which comes from the wave equation

$$\frac{\partial^2 \varphi}{\partial t^2} = a^2 \Delta \varphi, \quad (2)$$

when we assume that  $\varphi$  contains a simple harmonic function of the time, the function  $V$  depending upon a single parameter  $q$ . If this is the case we have